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THE CHEMISTRY OF ORGANOPHOSPHORUS COMPOUNDS AND THEIR USE

- USSR -

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FOREWORD

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[The following is a translation of an article by Academician B. A. Arbuzov in Vestnik Akademii Nauk SSSR (Bulletin of the Academy of Sciences USSR), Vol XXX, No 3, Moscow, 1960, pages 103-105.]

The second conference for the chemistry and use of organophosphorus compounds was held in Kazan' from 26 November to 1 December 1959.

The chemistry of the organic derivatives of phosphorus has in recent times greatly attracted the attention of researchers. The increased interest in this only recently isolated area of organic chemistry is explained by many reasons. Such problems, fundamental to the theory of organic chemistry, as tautomerism, intramolecular rearrangement, addition to the multiple bond, and many others are being studied in these compounds.

The discovery of the most vigorous physiological activity of entire groups of organophosphorus compounds has evoked the increased attention of physiologists, physicians, veterinarians, agronomists, toxicologists, entomologists, and other representatives of the biological sciences.

With each year the use of organophosphorus compounds increases in the most varied areas of industry. These compounds are used as extractants for the recovery and separation of rare elements, as plasticizers for high-polymer products, hardeners, valuable additives to lubricants, and as flotation agents. In recent years there has appeared a new diversified area for the use of organophosphorus compounds -- the synthesis of phosphorus containing polymer materials possessing valuable properties.

The diversity of interests in organophosphorus compounds found repercussions in the work of the conference, which had attracted more than 400 chemists, physiologists, physicians, entomologists, and agronomists from 11 of the nation's cities. Results of the complex study of organophosphorus compounds undertaken in the USSR were discussed at the meetings of the three sections -- chemistry, physiological activity of organophosphorus compounds, and plant protection. A total of 122 reports were heard at the conference.

The paths of development of the chemistry of organophosphorus compounds for the past five years were illuminated in the report of B. A. Arbuzov. He indicated the tremendous achievements in this field. Results of the study of the paths of synthesis of organophosphorus compounds, which a short time ago were only of theoretical interest, have laid a basis for industrial methods of preparation of organic derivatives of phosphorus, by means of which a large number of such methods have been worked out at the present time. In recent years interest has increased in the phosphines and heterocyclic compounds containing phosphorus; there has been an expansion in the application of a variety of physical methods for the investigation

of the structure of organophosphorus compounds. These compounds have begun to be employed for the synthesis of organic compounds not containing phosphorus (polypeptides, carotinoids). As an example of organophosphorus compounds possessing physiological activity the lecturer introduced an insecticide which assured complete liquidation of fly maggots in concentrations of 1 x 10^{-6}% and even preparations possessing anti-tumoral effects. In conclusion the lecturer emphasized the great contribution which soviet researchers have made to the chemistry of organophosphorus compounds.

As an example of organophosphorus compounds M. I. Kabachnik selected the central theoretical problem of chemistry today -- the effect of a molecule's structure on its reactivity. Although this effect not long ago was looked into in a qualitative manner, and then only superficially, now, thanks to the use of Hammett's equation (with well-known limitations) it can be quantitatively evaluated. From much experimental material the speaker analyzed the question of the relationship of the ionization constant of various acids of phosphorus with their structure. He showed that, knowing the number of sigma groups attached to pentavalent phosphorus, the ionization constant of oxyacids of phosphorus, even of its monothio acids, can be determined with great accuracy. The report examined the adaptability of Hammett's equation for the resolution of the question of the effect of the nature of the solvents on the equilibrium constant of acids of pentavalent phosphorus.

The feasibility of quantitative evaluation of the effect of substituents on the reaction rate and equilibrium conditions of certain types of organophosphorus compounds was demonstrated.

In the summary report of Ye. L. Gefter, attention was focused on the use of organophosphorus compounds for the manufacture of high-polymer compounds. The addition of phosphorus in polymers makes them incombustible, and in a group of instances increases their thermal stability. Polymers containing the phosphoric acid group are excellent ion-exchange resins -- cationites having high selective action. Some organophosphorus compounds can be used as polymerization catalysts.

The report of M. Ya. Mikhel'son, E. V. Zeymal', and N. K. Fruyentov was devoted to a review of the chemical mechanism for the reaction of organophosphorus compounds with cholinesterases, in connection with this, what lies at the base of the physiological activity of the examined class of compounds is their ability to inactivate the cholinesterases. Certain rules, correlating this ability with the structure of organic derivatives of phosphorus, can be comprehended, proceeding from the distribution of electrons in a molecule of that compound. On the basis of much experimental evidence it was shown that the physiological activity of organophosphorus compounds is affected by their transformations in the organism, their distribution among different organs, and among different parts of the cell.

In the chemical section much attention was allotted to questions of the tautomerism of organophosphorus compounds (T. A. Mastryukova, S. T. Ioffe, V. S. Vinogradova, V. A. Gilyarov.) Numerous reports were

concerned with synthesis studies for the derivation of organic derivatives of various types. (A. V. Kirsanov, N. N. Mel'nikov, I. F. Lutsenko, A. N. Pudovik, G. Kh. Kamay, B. A. Arbuzov, V. S. Abramov, A. I. Razumov, et. al.)

As distinguished from the first conference on organophosphorus compounds, a great number of communications now concerned themselves with the synthesis of organophosphorus compounds capable of polymerization and polycondensation (V. V. Korshak, M. I. Kabachnik, T. Ya. Medved', G. Kh. Kamay, Ye. V. Kuznetsov, G. M. Vinokurova) and the derivation, from these, of polymer products, (V. V. Korshak, G. S. Kolesnikov et al.) P. I. Sanin brought forward interesting data concerning organophosphorus compounds as additives to lubricating oils. In the reports of A. I. Kreshkov and M. G. Voronkov syntheses were investigated for compounds containing phosphorus and silicon. A special session of the chemical section was devoted to the synthesis of ethylenimine derivatives of phosphorus, specifically possessing the anti-tumoral effect, and their biological activity. (A. A. Kropacheva, and S. I. Sergiyevskaya, L. Kh. Protsenko, N. P. Grechkin).

At sessions of the section on the physiological activity of organophosphorus compounds much attention was allotted to the study of the interrelations of their chemical structure and biological activity. (V. A. Yakovlev, Yu. S. Kogan, I. A. Frankova, G. F. Rzhevskaya, I. V. Zaikonnikova, L. S. Afonskaya), and also to the effect of organophosphorus compounds on nerve-muscle transmission (N. K. Fruyentov, V. N. Asekritova, V. V. Mozhukhina, I. M. Rakhmatullin, V. M. Sirotkin). At a separate session the application of organophosphorus compounds for the treatment of glaucoma (V. M. Krasnova, Z. M. Osipova, G. I. Timinskaya) and the employment of such compounds as growth stimulating medium were examined (L. V. Chugunova, N. A. Korchagina). Data concerning the use of organophosphorus compounds for the treatment of experimental trichophytosis in animals offered special interest (I. D. Neklesova). The reports heard have indicated that the field of study of the effect of organophosphorus compounds on biological objectives has recently expanded considerably.

In the section on plant protection the investigation of the cholinergic system of insects and of the mechanism of insecticidal activity of organophosphorus compounds were of interest (A. K. Voskresenskaya). Interesting data were provided concerning the biological effect of organophosphorus compounds on agricultural pests as well as on crops and soil microflora. (A. M. Alekseyev). Of some importance are the results of the use of organophosphorus compounds for the protection of grain crops and cotton (P. V. Sazonov, Ye. N. Kozlova).

In the resolutions of the conference it was emphasized that the chemistry of organophosphorus compounds has survived a period of intense growth in the USSR, added to which is the very real significance presented by a new and broad direction -- the chemistry of phosphorus-containing high polymer compounds. However, exploitation of the valuable organophosphorus compounds produced is taking place much too slowly, and will be completed only in extremely rare cases. Participants in the conference acknowledged the need for convening scientific conferences on the chemistry and use of organophosphorus compounds at least once every three years.

The conference recommended the expansion in every way of work in the field of the biochemistry, physiology and toxicology or organophosphorus compounds.

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